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TITLE : METHOD FOR SURFACE-TREATING VULCANIZED RUBBER MOLDING

ABSTRACT : PROBLEM TO BE SOLVED: To obtain a molding surfaced with a tack-free, low-frictional-resistance, nonsticky layer by bringing a vulcanized rubber molding into contact with a vaporized silane-type coupling agent compound in a sealed container.

SOLUTION: The silane-type coupling agent is exemplified by vinyltrimethoxysilane or vinyltriethoxysilane and is desirably a lower alkoxysilane-type coupling agent compound. The silane coupling agent compound can be easily vaporized by heating, and simultaneously performs curing and a reaction with the functional groups of the rubber to form a nonsticky layer having high adhesion to the rubber. The heating is performed at a temperature of 100-250°C and depends on the type of the coupling agent used. The treatment apparatus entirely consists of a sealed container and a heater and does not need any special apparatus. The formed surface treatment layer provides surface tack-freeness and reduced frictional resistance and prevents the blocking among the vulcanized rubber moldings. Because of its ability to reduce the frictional resistance of a sliding part, it is useful as a sealing material for an O ring, etc.

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(54) 【発明の名称】 加硫ゴム成形品の表面処理方法

(57) 【要約】

【課題】 表面粘着性がなく、摩擦抵抗の低い耐久性非粘着層を表面に形成せしめる加硫ゴム成形品の表面処理方法を提供する。

【解決手段】 加硫ゴム成形品を密閉容器中で気化したシラン系カップリング剤化合物と接触させ、加硫ゴム成形品の表面を処理する。

## 【特許請求の範囲】

【請求項1】 加硫ゴム成形品を密閉容器中で気化したシラン系カップリング剤化合物と接触させることを特徴とする加硫ゴム成形品の表面処理方法。

【請求項2】 請求項1記載の方法で表面処理された加硫ゴム成形品。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、加硫ゴム成形品の表面処理方法に関する。更に詳しくは、表面粘着性がなく、摩擦抵抗の低い加硫ゴム成形品を与える表面処理方法に関する。

## 【0002】

【従来の技術】加硫ゴム成形品は、それ自身が粘着性を有するため、成形品同士のブロッキングにより、取扱作業性の低下、装置への装着もしくは組込作業性の低下、装置への装着もしくは組込み後にゴム成形品表面に接触する相手材への粘着、摩擦抵抗による作動不良等をひき起す原因ともなっている。

【0003】このような加硫ゴム成形品の表面粘着防止方法としては、成形品の表面にSi含有化合物等の塗液を噴霧、浸せき等の手段により塗布する方法が実用化されている。しかしながら、この方法は塗布ムラを生じさせる場合があり、成形品表面に安定した粘着防止効果を付与させることができないばかりではなく、塗布工程を必要とするので、成形品の加工効率を低下させる結果となり、コストが上昇するという問題がある。また、複雑な形状のものや円筒状のものの内面側などには、均一な塗布が困難である。

【0004】特公平6-39147号公報には、高真空減圧装置によりプラズマ発生装置を減圧してシランガスをボンベより導入し、プラズマ照射によってフッ素系重合体表面にポリシロキサン硬化層を形成させることにより、表面粘着性を防止する方法が記載されている。しかしながら、このような処理をするには、高価な装置を必要とするばかりではなく、1回の処理量を多くすることも困難であり、更に常温でシランガスを取扱うための危険性や人体への悪影響などもみられる。

## 【0005】

【発明が解決しようとする課題】本発明の目的は、表面粘着性がなく、摩擦抵抗の低い耐久性非粘着層を表面に形成せしめる加硫ゴム成形品の表面処理方法を提供することにある。

## 【0006】

【課題を解決するための手段】かかる本発明の目的は、加硫ゴム成形品を密閉容器中で気化したシラン系カップリング剤化合物と接触させ、加硫ゴム成形品の表面を処理する方法によって達成される。

## 【0007】

【発明の実施の形態】本発明方法によって表面処理され

る加硫ゴム成形品としては、フッ素ゴム、アクリルゴム、ニトリルゴム、クロロプレンゴム、EPDM等の合成ゴムまたは天然ゴムの加硫成形品である。

【0008】これらの加硫ゴム成形品は、密閉容器中で気化したシラン系カップリング剤化合物と接触せしめる。シラン系カップリング剤化合物としては、例えばビニルトリメトキシシラン、ビニルトリエトキシシラン、ビニルトリアセチルシラン、 $\alpha$ -メタクリロキシプロピルトリメトキシシラン、 $\alpha$ -グリシドキシプロピルトリメトキシシラン、 $\beta$ -(3,4-エポキシシクロヘキシル)エチルトリメトキシシラン、 $\gamma$ -メルカプトプロピルトリメトキシシラン、 $\beta$ -メルカプトエチルトリエトキシシラン、 $\alpha$ -クロロプロピルトリメトキシシラン、 $\alpha$ -クロロプロピルトリエトキシシラン、ビニルトリクロロシラン、 $\alpha$ -アミノプロピルトリメトキシシラン、 $\alpha$ -アミノプロピルトリエトキシシラン、N- $\beta$ -(アミノエチル)- $\alpha$ -アミノプロピルトリメトキシシラン、N- $\beta$ -(アミノエチル)- $\alpha$ -アミノプロピルトリエトキシシラン、N- $\beta$ -(アミノエチル)- $\alpha$ -アミノプロピルメチルジメトキシシラン、 $\alpha$ -(ジエチレントリアミノ)プロピルトリメトキシシラン、 $\alpha$ -ウレイドプロピルトリエトキシシラン、イミダゾリントリエトキシシラン、 $\alpha$ -[N-( $\beta$ -メタクリロキシエチル)-N,N-ジメチルアンモニウム(クロライド)]プロピルトリメトキシシラン、スチリルジアミノシラン、アミノジ(トリメチル)シラン、(3-ジアミノメチルチオプロピル)シラン、ビス(3-トリエトキシシリルプロピル)テトラスルファン、パーフルオロアルキルシラン等が用いられ、好ましくは低級アルコキシ基を有するシラン系カップリング剤化合物が用いられる。

【0009】これらのシラン系カップリング剤化合物は、加熱により気化し易く、加熱されているため硬化と同時にゴムの官能基と反応し、ゴムとの間に強固な密着性を有する非粘着層を表面処理層として形成させる。加熱は、用いられるシラン系カップリング剤化合物の種類に応じて、約60~300℃、好ましくは約100~250℃の温度で行われる。

【0010】これ以下の加熱温度では、気化やミスト化が不十分となり、処理された加硫ゴム成形品表面の目付量が少なかったり、あるいは密閉容器の上側と下側とでは目付量に差が生じたりする。一方、これ以上の加熱温度が用いられると、ゴムの熱劣化を生ずるようになる。

【0011】処理時間は、用いられるシラン系カップリング剤化合物の揮発性や反応性、使用量（一般には、約0.5~50g/m<sup>2</sup>程度）、処理温度、密閉容器の大きさなどによって異なり、処理温度が高い程処理時間は短くなる傾向を有するが、一般には約0.5~24時間程度である。

【0012】このようにして行われる表面処理に用いられる密閉容器としては、上記温度範囲で行われるシラン系カップリング剤化合物に不活性でありかつ外気との入

れ換えがなく、気化したガスやミストが洩れない程度の密閉性を有していれば良く、特殊な耐圧構造を必要としないので、使用温度によって金属製あるいは樹脂製の容器を使用することができる。これに対して、密閉容器を用いることなく、大気中で同じ化合物による処理を行った場合には、所期の目的を達成することができない。

#### 【0013】

【発明の効果】本発明方法は、次のような特徴を有する。

(1) 溶剤などを用いることなく、複雑な形状の加硫ゴム成形品に均一な非粘着性表面処理層を形成させることができる。

(2) 処理装置として用いられるものは、密閉容器と加熱装置のみで、特別な装置を必要とはしない。

(3) 密閉容器の容量を大きくすれば、1回の処理量を多くすることは容易であり、処理費用の削減も可能であ

る。

(4) 加硫ゴム成形品表面に化学的に結合したシリコーン構造が形成されるので、そこに形成された表面処理層は耐久性の点ですぐれている。

(5) 形成された表面処理層は、加硫ゴム成形品表面の粘着防止や摩擦抵抗を低減させ、また加硫ゴム成形品同士のブロッキングを防止させる。

(6) 表面処理層は、ゴムと強固に密着し、硬化しているため、高温下で圧着しても粘着性がなく、また耐溶剤性も良好である。

(7) 摺動部分の摩擦抵抗を低減させるので、Oリング、Dリング、角リング、Vパッキン、オイルシール、ガスケット等のシール材に有効に適用される。

#### 【0014】

【実施例】次に、実施例について本発明を説明する。

#### 【0015】

##### 実施例1

フッ素ゴム(デュポン社製品バイトンA-100)	100重量部
MTカーボンブラック	15 "
酸化マグネシウム	3 "
水酸化カルシウム	5 "
ビスフェノールAF	2 "
トリフェニルベンジルホスホニウムクロライド	2 "

【0016】以上の各配合成分をニーグおよびオープンロールを用いて混練し、混練物について170℃、20分間のプレス加硫を行ない、厚さ2mmのシートおよびJIS B-2401に規定されたOリング(内径24.4mm、太さ3.1mm径；呼び番号G30)をそれぞれ加硫成形した。

【0017】これらの加硫ゴム成形品をn-ヘキサン中に浸せきして、ゴム表面の付着物除去を行った後、容量200mlのステンレス鋼製密閉容器(内径40mm、高さ200mmの円筒状容器であって、上部に蓋のあるネジ込み式のもの

の)の中に、30×150mmの大きさのシートおよびアーグリシドキシプロビルトリメトキシシラン0.1g、またはOリング3個およびアーグリシドキシプロビルトリメトキシシラン0.05gを入れ、180℃で3時間加熱処理した後密閉容器を水冷し、室温下で容器を開放して、表面処理されたシートまたはOリングを取り出した。

【0018】このようにして表面処理された加硫ゴム成形品について、次の各項目の試験が行われた。

摩擦試験：新東科学製表面性試験機を用い、ASTM D-1894に準じて、シートの動摩擦係数を測定

(試験条件) 相手材：直径10mmのクロム鋼球製摩擦子

移動速度：50mm/分

荷重：50g

金属との粘着試験：40℃、95%RHの恒温恒湿槽中で、シートとアルミニウムの端部同士を12.5±0.5mmの長さで重ね合せ、0.15Kg/cm<sup>2</sup>の面圧で5時間圧着した後、室温下でJIS K-6850引張せん断接着強さ試験法に従って、引張せん断接着強さ試験片の引張強さを測定

シート同士の粘着試験：金属との粘着試験法をシート同士に適用し、試験片の引張強さを測定

金属との高温粘着試験I：試験片を120℃の恒温槽中でアルミニウム板と面圧0.15Kg/cm<sup>2</sup>で5時間圧着した後、金属との粘着試験法を適用し、試験片の引張強さを測定

金属との高温粘着試験II：OリングをJIS K-6301圧縮装置(圧縮相手面アルミニウム)で25%圧縮した状態で、120℃の恒温槽中に5時間、次いで室温下に1時間放置した後、圧縮装置との粘着の有無を目視で観察

表面処理層の耐溶剤性試験：ウェスに各種溶剤を浸み込ませ、シート表面を10

回軽く拭き取り、表面処理層の剥離の有無を目視で観察

【0019】実施例2

実施例1において、 $\gamma$ -グリシドキシプロピルトリメトキシシランの代りに、それぞれ同量の $\gamma$ -メタクリロキシプロピルトリメトキシシランが用いられた。

【0020】比較例1

実施例1において、シートまたはOリングに $\gamma$ -グリシドキシプロピルトリメトキシシランをスプレーで塗布した後、180℃の電気炉で3時間の加熱処理を行った。

【0021】比較例2

比較例1と同様に、シートまたはOリングに $\gamma$ -アミノプロピルトリメトキシシランをスプレーで塗布した後、180℃の電気炉で3時間の加熱処理を行った。

ロピルトリメトキシシランをスプレーで塗布した後、180℃の電気炉で3時間の加熱処理を行った。

【0022】比較例3

実施例1において、シートまたはOリングに $\gamma$ -アミノ変性シリコーンオイル(信越化学製品KF393)をスプレーで塗布した後、180℃の電気炉で3時間の加熱処理を行った。

【0023】以上の各実施例および比較例での試験結果は、次の表に示される。

表

試験項目		実-1	実-2	比-1	比-2	比-3
摩擦試験		0.1	0.2	0.5	0.2	0.1
金属との粘着試験	(Kg/cm <sup>2</sup> )	0	0	0.3	0.4	0.5
シート同士の粘着試験	(Kg/cm <sup>2</sup> )	0	0	0.4	0.5	0.8
金属との高温粘着試験I	(Kg/cm <sup>2</sup> )	0	0	1.0	1.0	0.8
金属との高温粘着試験II (粘着の有無)		なし	なし	あり	あり	あり
表面処理層の耐溶剤性試験(剥離の有無)						
メタノール		なし	なし	なし	なし	あり
トルエン		なし	なし	あり	あり	あり
イソオクタン		なし	なし	あり	あり	あり

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<b>(21) International Application Number:</b> PCT/US84/01879 <b>(22) International Filing Date:</b> 16 November 1984 (16.11.84)  <b>(31) Priority Application Number:</b> 552,316 <b>(32) Priority Date:</b> 16 November 1983 (16.11.83) <b>(33) Priority Country:</b> US  <b>(71)(72) Applicant and Inventor:</b> ROBBART, Edward [US/ US]; 15 Emerson Place, Boston, MA 02114-2250 (US).  <b>(74) Agents:</b> COHEN, Jerry et al.; 33 Broad Street, Boston, MA 02109 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BE (Eu- ropean patent), BR, CH (European patent), DE (Eu- ropean patent), DK, FI, FR (European patent), GB (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU.		<b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVEMENTS IN THE COATING OF CELLULOSIC BASE STOCKS AND THE PRODUCTS THEREOF  <b>(57) Abstract</b>  In a method of coating webs of cellulosic base stocks wherein a coating material is applied to the web of the base stock so as to improve the properties thereof, the improvement comprising, prior to said coating, treating the web with vapors of silane which react with hydroxyl groups in the cellulosic base stock to form a deposit of siloxane and polymers thereof on and integral with said web of cellulosic base stock.		

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IMPROVEMENTS IN THE COATING OF CELLULOSIC  
BASE STOCKS AND THE PRODUCTS THEREOF

FIELD OF THE INVENTION

This invention relates to improvements in the coating of cellulosic base stocks and to the novel products obtained thereby. More particularly, the present invention is directed to improvements in the coating of webs of cellulosic base stocks by treating the webs with vapors of an organosilicon halide prior to said coating and to the resulting novel products.

BACKGROUND OF THE INVENTION

The development of coated papers has been marked by innovations relating to method and apparatus of applying liquid coatings as a film to a moving web; by the systematic exploration of possible coating formulations; and by the development of various techniques to dry the coating applied.

A crucial consideration in this effort has been the base stock to be coated and here effort has focused on existing techniques for modifying the characteristics of paper to optimize the operation. With the substantial technical advances that have been made in the other areas of coating methodology, at this point it might be observed that base stock preparation is the crucial area needing consideration.

Coatings are applied to paper or paperboard for a wide variety of purposes. For publication grades of paper or paperboard, enhancement of surface appearance is achieved by formulations using a pigment, a binder, and water. Other agents may be added for brightnees, enhanced flow properties, and prevention of foam.

For boxboard, multiwall bag, and some other paper grades, a plastic coating such as polyethylene





coating is widely employed to provide a measure of release, gloss, water repellency, and inhibition of moisture vapor transmission. Waxes are sometimes employed for similar purposes and to provide rigid-when-wet characteristics for corrugated containers.

Some specialty coatings are silicones, applied as water based emulsions, dissolved in solvents, or 100% solids; coatings of carbonless solution; zinc oxide coatings; and others which serve particular functions such as imparting release, image transfer under pressure, and electrostatic image transfer respectively.

There are an enormous variety of coatings. However, these present very similar problems in terms of base stock requirements. One essential base stock characteristic is evenness of moisture profile. A sheet with uneven moisture content will tend to accept coating unevenly. Another essential base stock characteristic is adequate wet strength. A sheet with insufficient wet strength, will weaken as the web contacts a liquid coating, and may break causing costly downtime and waste. Another essential base stock characteristic is capability of bonding to the coating solution. This bond is a key factor in producing durable coating. Finally, perhaps the most essential base stock characteristic is holdout to the coating solution. The rate and extent to which the base stock absorbs the coating solution affects pickup of the coating, sheet breaks, drying, speed of operation, and quality of finished product.

The interaction between the base stock and the coating solution is the heart of the coating process. An inadequacy of base stock can sometimes be adjusted through modification of the coating solution, method, or both. The direction of approach in solving these problems is to some degree dependent on whether



the fibrous component of the final product is more costly on a weight basis or whether the coating component is the more costly. As the final product will, in most cases be sold by weight, much research and development effort has been focused on enhancement of technique to achieve reduction of fibrous component or coating component without mitigating essential characteristics of the final product.

#### SUMMARY OF THE INVENTION

The present invention is based on the finding that treating webs of cellulosic base stocks with vapors of silanes to modify the web prior to coating of the web with a coating material normally employed to improve the properties of the web, significantly enhances the coating process. The silane vapor treatment permits minimal usage of coating material while producing uniformity of effect by virtue of diffusion of the vapor across the web wherein it reacts with hydroxyl groups in the cellulose (and with hydroxyl groups of any moisture present) to form a deposit of siloxane and polymers thereof which is chemically bonded to and therefor integral with the cellulosic webs. In particular, it has been found that exposure of cellulosic sheet to vapors of silanes can impart needed hold out, wet strength, release and other characteristics as well as greatly facilitate the subsequent coating operation.

Thus, the process of the invention provides as articles of manufacture cellulosic substrates having a base layer coated on at least one side with a layer of a coating material to improve the properties thereof, said base layer being obtained by treating the cellulosic substrate with vapors of a silane which react with hydroxyl groups in the cellulosic substrate to form a deposit of siloxane and polymers thereof on and integral with the cellulosic substrate.



There are a number of specific benefits derived from treating a web with vapors of the silanes of the invention prior to coating. Treatment allows elimination of costly and less effective sizing agents. Treatment enhances wet strength and inhibits capillary action and thus reduces sheet breaks and downtime during coating. Treatment upgrades and makes uniform the base stock and thus allows greater selection of furnish in making the base stock. Treatment increases holdout to the coating solution and thus enables a reduction in coat weights needed to achieve identical surface characteristics. Treatment reduces moisture absorption by the sheet during coating and thus reduces energy requirements for subsequent drying and allows increased speed of operation. Treatment allows greater versatility in coating formulations as problems of absorption, binder migration and matting are to a degree obviated. Treatment allows greater range in base stock selection as problems of holdout and wet strength are easily remedied.

To generalize, in the case where the fibrous component is the more costly the treatment may be used to allow use of lighter weight base stocks, or stock which is cheaper to produce or finish, and which is then upgraded by the treatment. In the case where the coating component is the more costly, treatment may be used to reduce the amount of coating by holding it to the surface, and may thereby further reduce drying requirements and enable faster processing.

The specific benefits conferred will vary with the specific coating operation. In every case a base stock more suitable for coating is produced by the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The treatment of the webs of cellulosic base



stocks with vapors of silanes can be effected, for example, by using the process described in U.S. Patent No. 3,856,558 and U.S. Patent No. 4,399,479, both of which are hereby incorporated by reference. According to these processes cellulosic materials having a moisture content of below 10% by weight, preferably below 7% by weight are contacted with the organosilicon halide. Cellulose materials having moisture contents in excess of 7% may be heated to remove surface moisture. Alternatively, such materials may first be frozen in accordance with the teachings of U.S. Patent No. 4,339,479. A moisture content of up to about 7 weight percent in the cellulosic material is preferred in those instances wherein the cellulosic material is not contacted in its cold or frozen state.

The contact time of the cellulosic material and the organosilicon halide is in all cases sufficient to effect siloxane formation and will vary depending upon the temperature of the cellulosic material and organosilicon halide vapor, the concentration of the organosilicon halide in the contacting atmosphere, the pressure within the reaction zone and the moisture content of the cellulosic material. Contact times ranging from .1 second up to 2 have been utilized successfully.

The temperature of the organosilicon halide is sufficiently high to effect reaction between the organosilicon halide and hydroxyl groups on the cellulosic material and any moisture present to form siloxane and/or polysiloxane within the claimed contact time but not so high as to degrade the cellulose at the contact time employed. Suitable temperatures range from 50°F, to about 200°F.

Generally, when employing higher temperatures, shorter contact times are employed and



conversely, when employing relatively low temperatures, longer contact times can be employed. Furthermore, the concentration of the organosilicon halide in the atmosphere through which the cellulosic material is passed can be varied up to the saturation level of the atmosphere for the organosilicon halide and, if employed, a solvent for the organosilicon halide. The concentration of the organosilicon halide can range up to the saturation level of the atmosphere but should not be so low as to require excessive contact times in order to effect the desired reaction and to render the cellulosic material water-repellent. Typically, the concentration of the organosilicon halide ranges from about 2% volume percent up to the saturation level of the atmosphere within the reaction zone.

The reaction zone is normally maintained under a slight negative pressure during the treating operation but the pressure therein can vary widely say from as low as 1 Torr up to about 760 Torr.

When a cellulosic material having a moisture content of below 2 weight percent is employed pursuant to one aspect of the present invention the contact time must be increased and the variables of organosilicon halide vapor temperature, concentration, and the contact chamber pressure are maintained so that the final pH of the cellulosic material rendered water-repellent does not fall below 2.5 and preferably not below 3.5. The range of conditions which will ordinarily be employed will fall in the following ranges:

Temperature of organosilicon halide: 50°F to 200°F

Temperature of cellulosic material: frozen to 200°F

Concentration of organosilicon halide: 2% to

saturation.

Again, within the ranges set forth conditions are selected and maintained so that the final pH of the cellulosic material does not fall below 2.5.

5 The suitable silanes useful in this process are those commonly employed in water repellency treatments of cellulosic materials. Suitable silanes include organosilicon halides and organoalkoxysilanes.

10 Illustration of organoalkoxysilanes which can be used are lower alkyl alkoxysilanes such as lower alkyl mono-, di- and tri- alkoxysilanes and mixtures thereof. Specific examples of lower alkyl alkoxysilanes are methyl trimethyloxysilane, dimethyl dimethyloxysilane, ethyl trimethyloxysilane, trimethyl  
15 ethoxysilane, etc. Useful organosilicon halides are described by Patnode in U.S. Patent No. 2,306,222, Norton, U.S. Patent No. 2,412,470, and in my earlier U.S. Patent Nos. 2,782,090, 2,824,778 and 2,961,338 which are incorporated herein by reference.  
20 Particularly suitable organosilicon halides are the lower alkyl silicon halides such as methylchlorosilanes, ethylchlorosilanes, butylchlorosilanes and propylchlorosilanes. Typically, however the silicon halides will be a  
25 mixture of dimethyldichlorosilane,  $(\text{CH}_3)_2\text{SiCl}_2$ ; methyldichlorosilane,  $\text{CH}_3\text{SiHCl}_2$ , and methyltrichlorosilane,  $\text{CH}_3\text{SiCl}_3$  which may contain silicon tetrachloride,  $\text{SiCl}_4$ .

30 The cellulosic material may be contacted with the vaporized organosilicon halide alone or together with a vaporized solvent for the organosilicon halide which solvent is inert both to the organosilicon halide and the paper being treated. It has been found  
35 that the presence of the solvent during the treatment step results in the formation of a treated cellulosic material having a higher pH as compared with a



cellulosic material which is treated with the same organosilicon halide without the solvent under equivalent reaction conditions. Representative suitable solvents include toluene, xylene, hexane, perchloroethylene, fluorinated hydrocarbons, or other non-reactive solvents in which the organosilicon halide may be dissolved. It has been found that as little as 10 mole percent solvent is effective but that larger concentrations of the solvents in the range of about 12 to 100 mole percent based upon the total mole of the organosilicon halide and solvent are preferred. A molar quantity ten times or more that of the organosilicon halide is effective. If desired, higher concentrations of the solvent can be employed. However, the presence of excessive concentrations of solvent effects a reduction of reaction rate and increases the expense of the solvent without a significant beneficial effect.

The silane vapors or the mixtures of silane vapors in solvent may be formed by bubbling air through the liquid silane or an admixture of the silane and solvent or more simply by dropping the liquid of the desired composition slowly onto a hot plate to generate vapors of the same molar composition as the liquid. Alternatively, an aerosol mixture may be employed as described in my U.S. Patent No. 2,824,778 which is incorporated herein by reference. When employing a solvent having a significantly different vapor pressure than the silane and when effecting vaporization by bubbling air, it is preferred that the solvent and silane be maintained as separate liquids in order to better control the composition of the vapors formed in the treating chamber.

The air to be mixed with the silane in the treatment step should contain as little water as



possible to avoid significant reaction of water in the air with the silane which results in the formation of by products such as hydrogen halide and reduction of the amount of silane that can react with the cellulosic material.

In instances where the moisture content of the cellulosic material to be treated is greater than about 10 weight percent, it may be desirable to subject the cellulosic material to a drying step prior to the treatment with organosilicon halide. The drying step need only be conducted at a temperature and a time sufficient to remove part of the surface moisture from the material while retaining at least about 2 weight percent moisture in the material. Heating to about 250°F. for from about 3 to 5 seconds is sufficient in most cases. The desirability or necessity of this step will depend upon such factors as the prevailing humidity on the day of treatment, the uptake of moisture by the material during manufacture and storage and the conditions of treatment. If desired, the cellulosic material treated with silane, either in the presence of or in the absence of a solvent, is further treated, upon removal from the silane treating step, to remove undesirable by-product such as hydrogen halide gas formed during the reaction prior to a substantial portion of it becoming dissolved by moisture in the cellulosic material. Generally, by product gas removal such as hydrogen halide gas removal can be effected by heating the cellulosic material, by applying suction to the cellulosic material or by passing the treated cellulosic material into contact with a moving stream of air.

Illustrative cellulosic base stocks treated pursuant to the present invention are cellulosic substrates such as paper of various grades,





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paperboard, wallboard, wood, textiles and the like.

5 The invention can be used to improve all coating processes wherein webs of cellulosic base stocks are coated with various coating materials to improve properties of the substrate such as surface characteristics, (e.g. brightness, gloss, pigmentation, smoothness, opacity, evenness of moisture profile, release, etc.), wet strength, water-repellency, adhesives, flame-retardation, image transfer under pressure, electrostatic image transfer, inhibition of moisture vapor transmission and the like. The various coating materials and formulations utilized to improve properties of cellulosic substrates such as those exemplified above are well known to those skilled in the art and need not be enumerated herein. See, for example, Looner, Joseph T., "Coated Papers", Handbook of Pulp and Paper Technology, Kenneth W. Britt, 1970, hereby incorporated by reference. Several illustrations of such coating materials and processes are given in the working examples below.

20 Conventional methods are employed for applying various coating materials to the cellulosic substrates and include flowing, spraying, dip coating, skin coating, spin coating, roll-type coating such as nip roll coating, reverse roll coating, trailing blade coating, etc., depending principally upon the substrate being coated.

25 The following examples are included to further illustrate the present invention.

#### EXAMPLE I

30 A sheet of bleached supercalendered Kraft paper, having a basis weight of 40 lbs. and a moisture content of 5% by weight is treated with vapors of methyldichlorosilanes at room temperature and atmospheric pressure for 5 seconds. The sheet is then



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coated with a commercial silicone release formulation at a coat weight roughly 20% of that normally required or about .12 lbs. per ream. The sheet is then cured in an oven at 300°F. for 60 seconds.

Subsequent testing with adhesives indicates the sheet has free release characteristics and is in every other way suitable for the same purposes a sheet with a higher weight of silicone coating would serve. In addition the sheet has superior bond to the coating.

#### EXAMPLE II

A sheet of machine glazed Kraft paper having a basis weight of 30 lbs. and a moisture content of 5% is exposed to vapors of the methyldichlorosilanes of Example I as described therein and then coated with a commercial silicone at a coat weight roughly corresponding to .5lbs per ream and then cured as in Example I. The sheet is found to have adhesive characteristics normally found on silicon-coated bleached supercalendered Kraft paper and for which far more expensive base stock with its enhanced holdout is required. For applications where evenness of caliper is not required, treatment appears to allow use of this far less expensive base stock.

The following example shows benefits of treatment in a continuous operation with a costly coating solution.

#### EXAMPLE III

A roll of fine paper having a basis weight of 20 lbs. and a moisture content of 5% by weight is exposed to vapors of a mixture of silanes comprised of 95% methyltrichlorosilanes, and 5% methyldichlorosilanes by weight. The exposure takes place on a continuous basis using a treating apparatus described in pending U.S. Application Serial No. 445,011 to Edward Robbart filed November 19, 1982,



hereby incorporated by reference. The sheet of paper enters the treating apparatus at a rate of 300 feet per minute so that the contact time is approximately .4 seconds. The treating unit is maintained at a slight negative pressure by the pull of an exhaust fan. The roll is subsequently coated with a commercial carbonless solution at a coat weight approximately 50% of that normally used. The solution is held to the surface of the web and copies made from the resulting paper are as clear as copies made on untreated sheets with heavier coating weights. The use of reduced coat weight allows faster operation as less drying is required.

#### EXAMPLE IV

A roll of newsprint having a basis weight of 30 lbs. and a moisture content of 4% is exposed to vapors of methyltrichlorosilanes on a continuous basis using the process and apparatus described in Example III. The roll is subsequently run through a blade coater at 2000 feet per minute and a coating of clay and starch applied. Breaks and other difficulties at high speed operation with this grade are not encountered. The finished product is found suitable as a publication grade.

#### EXAMPLE V

A roll of bleached board having a basis weight of 60 lbs. and a moisture content of 3.5% is exposed to vapors of 60% methyltrichlorosilanes, and 40% dimethyldichlorosilanes by weight. The exposure takes place on a continuous basis using the process and apparatus described in Example III. One side of the roll is subsequently coated with a 1 mil polyolefin, e.g. polyethylene, coating by extrusion. The roll is found suitable for foodboard applications normally requiring two-sided polyethylene coating. The release, water repellency and inhibition of



capillary action conferred by the silanes enhance one side, while the gloss and moisture vapor block from the polyethylene make the board as a whole suitable.



IT IS CLAIMED:

1. In a method of coating webs of cellulosic base stocks wherein a coating material is applied to the web of the base stock so as to improve the properties thereof, the improvement comprising, prior to said coating, treating the web with vapors of silane which react with hydroxyl groups in the cellulosic base stock to form a deposit of siloxane and polymers thereof on and integral with said web of cellulosic base stock.
2. A method according to Claim 1 wherein the cellulosic base stock is paper.
3. A method according to Claim 2 wherein said coating material is a paper sizing agent.
4. A method according to Claim 2 wherein said coating material is an adhesive.
5. A method according to Claim 2 wherein said coating material is a release agent.
6. A method according to Claim 2 wherein said coating material is a carbonless solution.
7. A method according to Claim 2 wherein the coating material is a synthetic plastic.
8. A method according to Claim 6 wherein the synthetic plastic is a polyolefin.
9. A method according to Claim 7 wherein the polyolefin is polyethylene.
10. A method according to Claim 1 wherein the silane is a lower alkyl silicon halide.
11. A method according to Claim 9 wherein said lower alkyl silicon halide comprises methylchlorosilane or a mixture of methylchlorosilanes.
12. In an article of manufacture wherein at least one side of a cellulosic substrate has applied thereto a layer of a coating material to improve the properties thereof, the improvement comprises



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providing a base layer for said coating material, said base layer being obtained by treating the cellulosic substrate with vapors of a silane which react with hydroxyl groups in the cellulosic substrate to form a deposit of siloxane and polymers thereof on and integral with said cellulosic substrate.

13. An article of manufacture according to Claim 10 wherein the cellulosic base stock is paper.

14. An article of manufacture according to Claim 11 wherein the coating material is a paper sizing agent.

15. An article of manufacture according to Claim 11 wherein said coating material is an adhesive.

16. An article of manufacture according to Claim 11 wherein said coating material is a release agent.

17. An article of manufacture according to Claim 10 wherein the silane is a lower alkyl silicon halide.

18. An article of manufacture according to Claim 17 wherein the lower alkyl silicon halide comprises methylchlorosilane or a mixture of methylchlorosilanes.

19. An article of manufacture according to Claim 11 wherein said coating material is a carbonless solution.

20. An article of manufacture according to Claim 11 wherein the coating material is a synthetic plastic.

21. An article of manufacture according to Claim 20 wherein the synthetic plastic is a polyolefin.

22. An article of manufacture according to Claim 21 wherein the polyolefin is polyethylene.



# INTERNATIONAL SEARCH REPORT

International Application No **PCT/US84/01879**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. <sup>3</sup> <b>C23C 11/00</b> U.S. Cl. <b>427/255.1, 255.6, 296, 316, 324, 326, 391, 392</b>														
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 20%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">U.S.</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">427/255.1, 255.6, 296, 316, 322, 324, 326, 391, 392, 411</td> </tr> </table> <div style="text-align: center; margin-top: 5px; font-size: small;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>6</sup></div>			Classification System	Classification Symbols	U.S.	427/255.1, 255.6, 296, 316, 322, 324, 326, 391, 392, 411								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; text-align: left;">Category <sup>5</sup></th> <th style="width: 60%; text-align: left;">Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup></th> <th style="width: 30%; text-align: left;">Relevant to Claim No. <sup>18</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,046,155 Published 24 July 1962 Reinke</td> <td style="vertical-align: top;">1-22</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,856,558 Published 24 December 1974 Robbart</td> <td style="vertical-align: top;">1-22</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,339,479 Published 13 July 1982 Robbart</td> <td style="vertical-align: top;">1-22</td> </tr> </tbody> </table>			Category <sup>5</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>	Y	US, A, 3,046,155 Published 24 July 1962 Reinke	1-22	Y	US, A, 3,856,558 Published 24 December 1974 Robbart	1-22	Y	US, A, 4,339,479 Published 13 July 1982 Robbart	1-22
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>•</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Date of the Actual Completion of the International Search <sup>1</sup></td> <td style="width: 50%; border: none;">Date of Mailing of this International Search Report <sup>2</sup></td> </tr> <tr> <td style="border: 1px solid black; padding: 5px; text-align: center;">24 December 1984</td> <td style="border: 1px solid black; padding: 5px; text-align: center;">14 JAN '85</td> </tr> <tr> <td style="border: none;">International Searching Authority <sup>1</sup></td> <td style="border: none;">Signature of Authorized Officer <sup>10</sup></td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">ISA/US</td> <td style="border: 1px solid black; padding: 5px;">             Michael R. Lusignan         </td> </tr> </table>			Date of the Actual Completion of the International Search <sup>1</sup>	Date of Mailing of this International Search Report <sup>2</sup>	24 December 1984	14 JAN '85	International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>10</sup>	ISA/US	 Michael R. Lusignan				
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